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Controlled co-crystallization of zeolites A and X

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Zeolites A and X were co-crystallized in controlled ratios from one synthesis gel. With increasing potassium content of the synthesis gel or increasing proportion of Na-Y seeds in a mixture of Na-Y and Na-A seeds, the ratio of zeolite X to zeolite A in the synthesis product increased.

Introduction

Zeolites are employed to a large extent as ‘detergent builders’ and water softeners. In 1999, 800,000 t of zeolites A and P were used for detergents.¹ In Europe, zeolites sometimes represent as much as 30 wt% of household laundry detergents, replacing environmentally unfriendly phosphates.

The aluminium content of zeolites provides their ion exchange capacity, since the net negative charge in the crystal-line framework at each aluminate site must be balanced by a compensating ion. Results reported in a patent issued to Union Carbide Corporation² indicate that, while zeolites Na-A and Na-X both have the capacity to ion exchange ‘hard water ions’, i.e., Ca^{2+} and Mg^{2+} , there is a synergistic effect when using mixtures of these two zeolites. The rates of ion exchange are greatly enhanced when using these mixtures compared to using either zeolite alone in the same solution. A mixture of 45 wt% zeolite Na-X with 55 wt% Na-A appears to have been the best combination to facilitate the removal of Ca^{2+} and Mg^{2+} ions from the authors’ test solutions.

Zeolite Na-X can have aluminium contents $n_{\text{Al}}/(n_{\text{Si}} + n_{\text{Al}})$ between 40 and 50% ($n_{\text{Si}}/n_{\text{Al}}$ ratios between 1.5 and 1.0). Zeolite X with an aluminium content close to 50% is called LSX (for low-silica zeolite X). While zeolite Na-LSX alone is better than either Na-A or Na-X alone in ion exchanging the hard water ions, it has been shown that there is also a synergistic effect when using mixtures of zeolites Na-LSX and Na-A in ion exchange studies with Ca^{2+} and Mg^{2+} ions.³ However, in that study, it was concluded that a mixture with 80 to 90 wt% zeolite Na-LSX and 10 to 20 wt% Na-A was the optimum for the manifestation of the synergistic effect (although the concentrations of Ca^{2+} and Mg^{2+} may have been different than in the previous study). The explanation given in that work was that the Ca^{2+} ions are exchanged preferentially into the Na-A zeolite, while the Mg^{2+} ions, apparently because of their larger size when hydrated, are exchanged without much competition by Ca^{2+} into the Na-LSX pores which are larger than the Na-A pores. Thus, there appears to be an incentive to modify detergents with some mixtures of zeolites, perhaps depending on the concentrations of Ca^{2+} and Mg^{2+} ions in local water systems.

The manufacturing process for molecular sieve zeolites requires separation of the solid product and mother liquor, washing of residual aluminosilicates from the solid product, and recycling of the mother liquor. Eventual accumulation of inorganic impurities from the reagents in the mother liquor requires that they be removed, either as a continuous purge or a periodic dumping of the entire fluid stream. Either remedy

to deal with accumulation of impurities requires downstream processing to concentrate the impurities and ultimate disposal or remediation of the wastes. Developing the ability to systematically produce controlled mixtures of zeolites Na-A and Na-LSX (or Na-X) for detergent applications will reduce the capital expense of building two manufacturing systems, requiring storage facilities for both zeolite phases, and dealing with the waste disposal from two zeolite manufacturing plants. In addition, exploiting the synergism would mean that less detergent would be required in cleaning applications and discharged to the public water system, thus reducing the impact on the environment.

The aim of this study was the controlled co-crystallization of mixtures of zeolites Na-A and Na-LSX for detergent applications. There have been several reports worth noting in which zeolites A and X have been observed to form simultaneously.^{4–9} While the second phase appeared as an impurity in those studies, and was not desired, we wished to take advantage of the conditions leading to the impurity phase to predictably produce zeolite mixtures. It has been shown that the co-crystallization of zeolites Na-A and Na-X is possible in the presence of triethanolamine^{6,7} or gluconate⁸ as aluminium complexing agents. However, the crystallization rate of the zeolite is inhibited by the depleted reservoir of unbound aluminium. This phenomenon gives rise to longer crystallization times and larger crystals, whereas for detergent applications small crystals (2 μm or smaller) are required. In addition, complexing agents can increase the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the products formed, which reduces the ion exchange capacity. Thus, the use of complexing agents was not appropriate for our aim. The starting point of our study was, hence, the very thorough work of Kühl.⁴ He performed syntheses of zeolite LSX with relatively small crystallite sizes in the presence of potassium and described in great detail the conditions under which zeolite LSX is formed in high purity or with impurities of zeolite A.

Experimental

The zeolite synthesis gels used in this study were prepared from sodium aluminate (Fisher Scientific, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, purified), NaOH (Aldrich, $\geq 97\%$), KOH (EM Science, $\geq 85\%$), sodium silicate solution (Fluka, $\approx 14\%$ NaOH, $\approx 27\%$ SiO_2), and deionized water. The reaction mixtures were charged to narrow-mouth plastic bottles (LDPE, Nalgene[®], 30 cm^3) and heated under static conditions at autogenous pressure.

The products were characterized by X-ray powder

diffraction at room temperature (Rigaku Geigerflex, $\text{CuK}\alpha$, 37.5 kV, 27.5 mA). The samples were run from 3.0 to 50.0 degrees 2θ with a step size of 0.05 degrees 2θ and a dwell time of 3 s. Each sample was hydrated over a saturated $\text{Ca}(\text{NO}_3)_2$ solution before analysis. For the determination of the proportion of zeolite X to zeolite A in the synthesis products, $m_X/(m_A + m_X)$, the average areas of the peaks with hkl (111), (311), and (331) for zeolite X and (200), (222), and (420) for zeolite A were calculated from 5 diffraction patterns of each sample. Afterwards, the 9 different area quotients of the peaks of zeolite X and A were determined and compared to the quotients obtained from standard mixtures of zeolites Na-A and Na-X. With linear regression, $m_X/(m_A + m_X)$ of the products was calculated from the double-logarithmic plots of the area quotients and zeolite X contents of the standard mixtures.¹⁰ The values given in the diagrams are the average from the 9 quotients with the standard deviation as the error bar.

The scanning electron micrographs were taken on AMRAY Model 1610 Turbo and Cambridge CAM SCAN 44 electron microscopes.

The rate at which the zeolite mixtures remove water hardness was determined by measuring the calcium and magnesium hardness remaining in a standard ‘hardness water’ after contact with the zeolites. The ‘hardness water’ contained $0.8 \text{ mmol dm}^{-3} \text{ CaCl}_2$ and $0.4 \text{ mmol dm}^{-3} \text{ MgCl}_2 \cdot 6\text{H}_2\text{O}$. 0.06 g of the respective hydrated zeolite mixture was stirred vigorously for 10 min with 100 cm^3 of the ‘hardness water’. The zeolite was removed immediately by fast vacuum filtration (about 30 s). The filtrates were collected, acidified and analysed for calcium and magnesium by titration. Calcium was titrated first with Na_2EDTA ($c = 0.1 \text{ mol dm}^{-3}$) at $\text{pH} = 12$ using

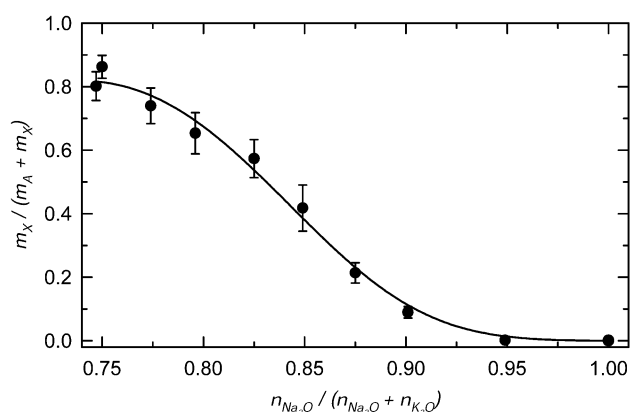


Fig. 1 Proportion of zeolite X to zeolite A in the synthesis products as a function of the sodium content of the synthesis gel.

calconcarboxylic acid†. After destroying the indicator with hydrogen peroxide (30 wt% aqueous solution) at 100°C , magnesium was titrated with Na_2EDTA ($c = 0.1 \text{ mol dm}^{-3}$) at $\text{pH} = 10$ using an indicator buffer tablet.

Results and discussion

For the first set of experiments, the following ratios were kept constant in the synthesis gel:

†The IUPAC name for calconcarboxylic acid is 3-hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthalenecarboxylic acid.

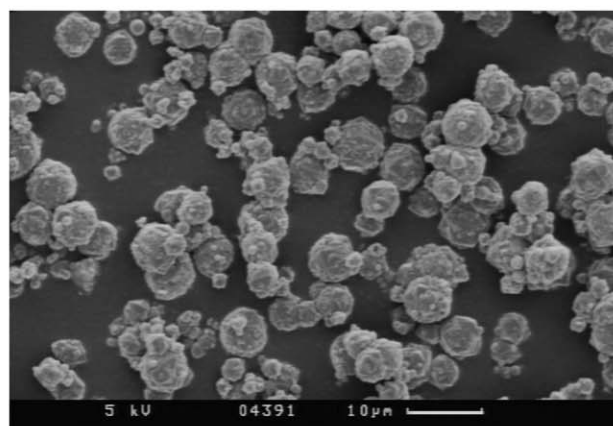
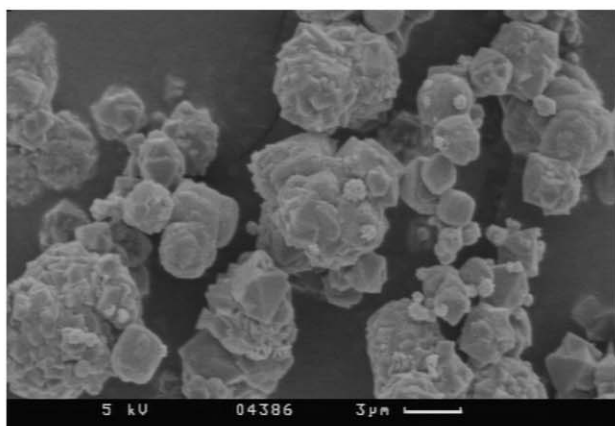
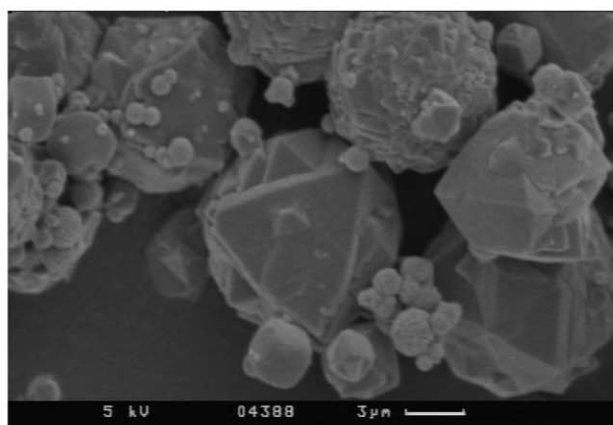
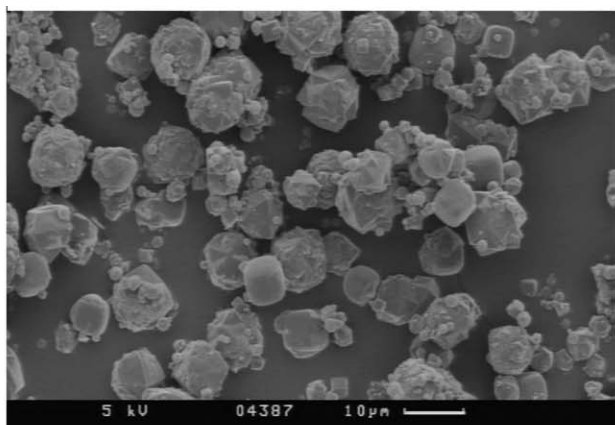


Fig. 2 Scanning electron micrographs of typical zeolite mixtures obtained in the unseeded systems (top left and top right), the seeded systems (bottom left) and of relatively pure zeolite LSX (synthesized after Kühl,⁴ bottom right). Note that the two upper photographs show the same zeolite mixture at different magnifications.

$$n_{\text{SiO}_2}/n_{\text{Al}_2\text{O}_3} = 2.0,$$

$$(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}})/n_{\text{SiO}_2} = 3.25, \text{ and}$$

$$n_{\text{H}_2\text{O}}/(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}}) = 26.$$

Only the ratio $n_{\text{Na}_2\text{O}}/(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}})$ was varied. All gels were first aged at 70 °C for 2 h. The crystallization was then performed for 3.5 h at 100 °C.

In Fig. 1, the proportion of zeolite X to zeolite A in the synthesis products, $m_X/(m_A + m_X)$, is displayed as a function of the sodium content of the synthesis gel, $n_{\text{Na}_2\text{O}}/(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}})$. It is obvious that by varying the sodium content of the synthesis gel, we were able to produce the whole range of mixtures of zeolite A and zeolite X. The proportion of zeolite X decreased with decreasing potassium content of the synthesis gel. From potassium-free gels, only zeolite A formed. This indicates that potassium is a template for the formation of zeolite X. The particle size of the crystallites also depended on the potassium content of the synthesis gels. The crystallite size in the zeolite mixtures decreased with decreasing potassium content from about 10 µm for zeolite X and about 6 µm for zeolite A to about 1 µm for both zeolites (*cf.* Fig. 2). This suggests that the nucleation rate increases with increasing sodium content of the synthesis gel.

In Fig. 3, an X-ray powder diffraction pattern of a typical zeolite mixture ($m_X/(m_A + m_X) = 0.57$) is displayed. From this and from scanning electron microscopy (*cf.* Fig. 2), it becomes obvious that the synthesis products contained besides zeolites A and X also to a small extent sodalite and amorphous products. The proportion of these by-products could only be determined with further calibration mixtures which were not prepared for this work. From a comparison of the area of the (110) sodalite peak of the synthesis products with a pure sodalite sample, we were, however, able to estimate that the sodalite content of all samples was smaller than 10%.

For the second set of experiments, synthesis gels with the following composition were prepared:

$$n_{\text{SiO}_2}/n_{\text{Al}_2\text{O}_3} = 2.0,$$

$$(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}})/n_{\text{SiO}_2} = 3.25,$$

$$n_{\text{H}_2\text{O}}/(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}}) = 26, \text{ and}$$

$$n_{\text{Na}_2\text{O}}/(n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}}) = 0.75.$$

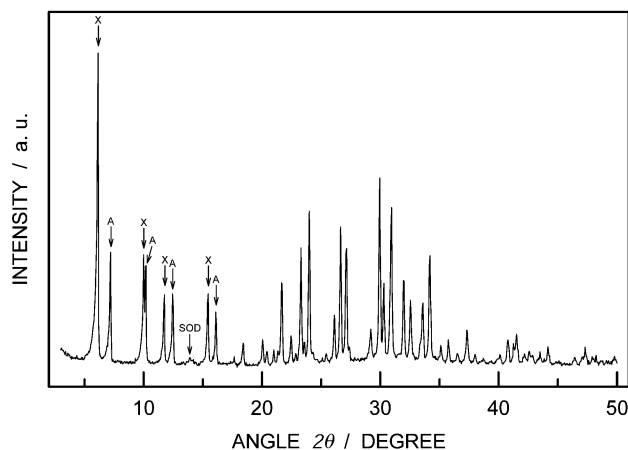


Fig. 3 X-Ray powder diffraction pattern of a zeolite mixture consisting of about 57 wt% zeolite X and 43 wt% zeolite A. The arrows in the low-angle region indicate the origin of the peaks (A = zeolite A, X = zeolite X, SOD = sodalite).

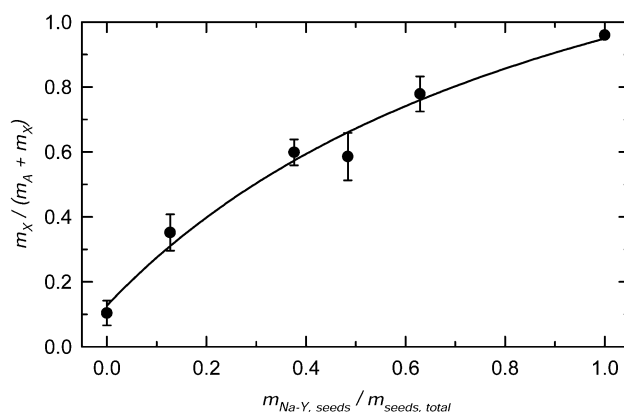


Fig. 4 Proportion of zeolite X to zeolite A in the synthesis products as a function of the proportion of zeolite Na-Y seeds in a mixture consisting of Na-Y and Na-A seeds.

To this mixture, zeolites Na-A and/or Na-Y¹¹ were added as seeds. After homogenization, the synthesis mixtures were aged at 70 °C for 1 h. The crystallization was then performed for 2.5 h at 100 °C.

Fig. 4 shows the proportion of zeolite X to zeolite A in the synthesis products as a function of the proportion of Na-Y seeds in a mixture consisting of zeolite Na-Y and Na-A seeds. Clearly, the addition of different seed mixtures enabled the controlled synthesis of the whole range of mixtures of zeolites A and X from *identical* synthesis gels.

In an additional experiment, seeds of Na-Y were added to a potassium-free synthesis gel (the synthesis gel was prepared in the same way as in the other seeding experiments except that KOH was replaced by NaOH). Even then, the product was virtually pure zeolite A. This supports the assumption made earlier that potassium is a template for the formation of zeolite X. Thus, the synthesis of mixtures of zeolites A and X is only possible in the presence of potassium.

In Fig. 5, the results of the ion exchange experiments with zeolites synthesized in unseeded systems are displayed. The ion exchange capacity for calcium was quite high and nearly independent of the content of zeolite X, indicating that the equilibrium value was reached. On average, about 17% of the calcium remained in solution after 10 min ion exchange. However, the ion exchange capacity for magnesium was low. One would expect that the ion exchange capacity for magnesium should increase with increasing content of zeolite X. This is indeed the case, but the slope is small. This is probably due to the zeolites containing potassium. With increasing content of zeolite X in the zeolite mixture, the potassium content of the mixture also increased, which lowered the ion exchange capacity.⁴ The ion exchange capacity for

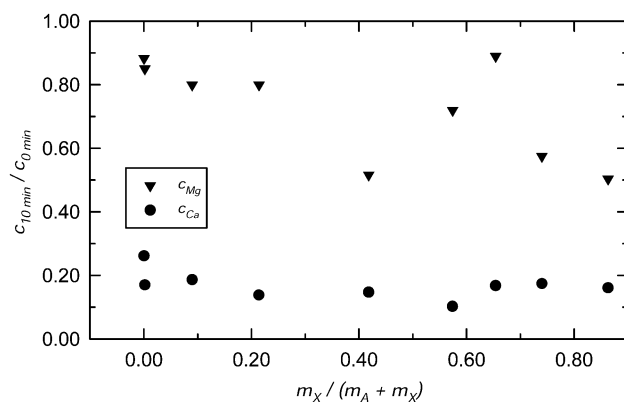


Fig. 5 Concentration of calcium or magnesium cations remaining in solution after 10 min ion exchange with different mixtures of zeolites A and X synthesized in unseeded systems.

magnesium was maximal for a mixture consisting of 86 wt% zeolite X and 14 wt% zeolite A. With this mixture, 50% of the magnesium remained in solution after 10 min ion exchange. No synergistic effect can be observed. This means that the zeolite mixtures produced cannot be employed as ion exchangers as such. For this application, it would be necessary to ion exchange potassium for sodium first.

Ion exchange experiments with the products of the seeded systems were not performed. It is, however, suspected that the ion exchange capacities of these products are comparably low since the potassium content in the synthesis gel was rather high.

Conclusions

A method has been developed for the controlled co-crystallization of zeolites A and X. By varying the potassium content of the synthesis gel or by adding specific seed mixtures consisting of zeolites Na-A and Na-Y, specific mixtures of zeolites A and X can easily be synthesized. However, the crystals obtained in this way have particle sizes between 1 and 10 μm . These sizes are actually too large for detergent applications. In addition, the crystals of zeolite X are multifaceted so that they would probably cling to fabric (*cf.* Fig. 2). Another problem is the low ion exchange capacity of the potassium-containing zeolites. The sodium ion exchange necessary for improving the capacity would presumably ruin the profit gained by directly synthesizing the zeolite mixtures.

In conclusion, the controlled co-crystallization is very interesting from a scientific point of view, but no industrial application is in sight yet.

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- 10 The intensities of the peaks depend on the $n_{\text{Si}}/n_{\text{Al}}$ and the $n_{\text{K}}/n_{\text{Na}}$ ratio of the sample. However, the effects should be the same for zeolites A and X so that the error should be small if area quotients are used.
- 11 Seeds of zeolite Na-Y (Mallinckrodt, particle size: 0.5 to 1.2 μm , crystallinity: 98%) were used, because they had the same particle size as the Na-A (Davison Molecular Sieves, particle size: 0.3 to 1.6 μm , crystallinity: 98%) seeds, *i.e.*, about 1 μm . Using mixtures of zeolites Na-A and Na-Y as seeds, 0.16 g of the seed mixture was added to 12.0 g synthesis gel. For the addition of only one type of seed crystals, 0.13 g Na-A and 0.25 g Na-Y were added to 12.0 g synthesis gel, respectively. Therefore, the Na-Y seeds corresponded to a maximum of 23% of all silicon atoms present in the synthesis mixture, and the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the product should increase only to an insignificant extent.